SnO$_{2}$ Thin Films Doped or Catalyzed with Mo: Structural and Gas Sensing Properties

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Tin oxide sensors are well known to be useful in detecting harmful toxic and inflammable gases, anyway sensor applicability requires optimal performances in terms of sensitivity, selectivity and stability.
Synergetic action of SnO_2–MoO_3 in promoting the dehydration-dehydronagenation of alcohol is known from catalysis science [1]. It's also known [2] that Mo doping of SnO_2 improves alcohols detection, leaves almost unaffected the ability to sense NO_2 [3] and lowers response to CO.

We studied morphological structural and sensing properties change of SnO_2 thin films as a function of Mo addition before and after annealing. In the first case the Mo is a doping material while in the second it's a catalyst because it's on the surface of SnO_2.

The SnO_2 thin films were produced by sputtering using the Rheotaxial Growth and Thermal Oxidation technique (RGTO). Starting from alumina substrate, Sn (about 3000 Å) was deposited in Argon atmosphere at 400 °C, then in the first case different amounts of Mo (8-16-24%, nominal values, in weight) were deposited at 300°C without breaking vacuum. After thin film deposition, samples were annealed in controlled atmosphere, for about 30 hours, at different temperatures: 500° C, 600°C and 700° C. In the second case a Mo layer (5 nm) and after an Au layer were deposited on SnO_2 RGTO films, already oxidized at 600°C.

From SEM analysis it was clear a deep modification in morphological structure of the film due to Mo addition and to annealing see figures 1-2. From EDXS analysis we observed a qualitative reduction of Mo content on annealed samples. This behavior is due to a partial evaporation of Molybdenum oxides during annealing.
Micro-Raman spectroscopy was used to map the samples surface and to see the distribution of the phases, even present in small quantity. On the first group of sample (doped with Mo) the Sn phase is detected for not annealed sample, whereas for the annealed ones the SnO_2 cassiterite peaks appear. Sn and Mo mixed oxides and MoO_3 are detectable in sample with Mo 8% not annealed (see fig. 3), MoO_3 is also detectable in all samples annealed at 500°C, but not in those annealed at higher temperature, confirming EDXS results.

Electrical measurements were performed at different temperatures, in presence of some typical gases like CO, NO_2, ozone and ammonia in order to evaluate influence of Molybdenum, as dopant and as catalyzer, on electrical properties as far as conductivity, gas response, response and recovery time. Molybdenum doping increases film conductivity in air, and samples annealed at higher temperature, so with less Mo, are more resistive. We observed that response to CO, NO_2, and ozone doesn't increase with Mo addition, while response to ammonia increases increasing Molybdenum content. Molybdenum catalyzing decreases film conductivity in air, improves response to NH_3 (see fig.4) and further it decreases response time, which, in the case of Mo-Au layer, is at least halved.

References:
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[3] A. Chiorino et al. "Preparation and characterization of SnO2 and MoO_x-SnO_2 nanosized powders for thick film gas sensors" Sensors and Actuators B 58 (1999) 338-349
[4] G. Sberveglieri "Classical and novel techniques for the preparation of SnO_2 thin films gas sensors" Sensors and Actuators B 6 (1992) 239-247

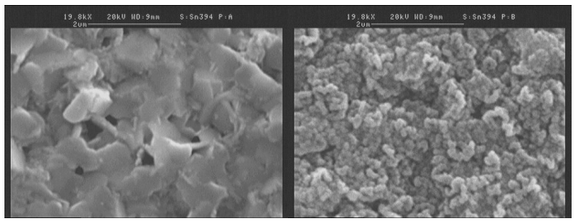

Figure 1 Sample with Mo 8% not annealed platelike structure is evident

Figure 2 Sample with Mo 8% annealed at 600°C morphology change during annealing is evident

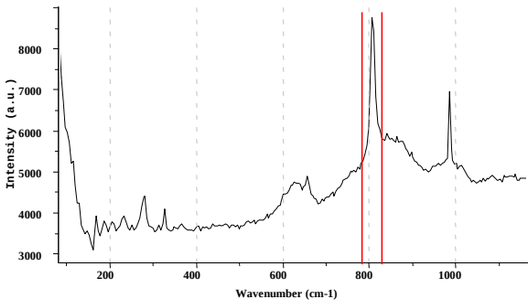

Figure 3 Raman spectrum collected in the mapped area of sample doped with Mo 8% and annealed at 500°C, MoO_3 peak is marked

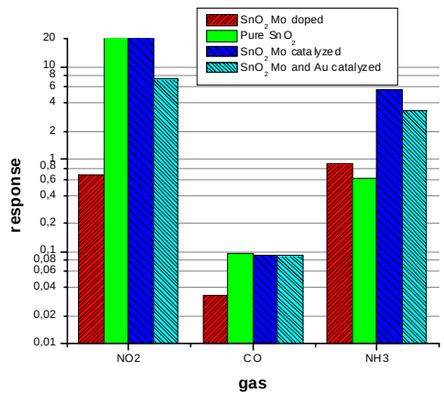

Figure 4 Comparison of responses to NO_2, CO and NH_3 of pure tin dioxide, Mo doped and catalyzed sensors